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SAMPLING PROFICIENCY TESTING AS A MEANS TO IMPROVE BOTH THE QUALITY OF SAMPLING, AND ESTIMATES OF MEASUREMENT UNCERTAINTY FROM SAMPLING

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1 THE ORIGINS AND DEVELOPMENT OF SAMPLING PROFICIENCY TESTING

Proficiency Testing (PT) has had a profound effect worldwide, on improving both the quality of analytical measurements, and estimates of their uncertainty. However, there has been an increasing realization that the measurement process usually begins at the time the primary sample is taken, rather than when the sample is delivered to a laboratory [1]. There was therefore, a clear rationale to extending the PT process to include sampling, in what is called a Sampling Proficiency Test (SPT). The measurement uncertainty arising from sampling (UfS) originates partly from heterogeneity of the analyte in the 'target' (the particular mass of material for which the sample is intended to represent), but also from variation in the manner in which the sample is extracted. Different sampling personnel implement their instructions somewhat differently, even when following a single protocol.

The concept of the SPT was first proposed in 1994 [2], and was first implemented on contaminated land in 1995 [3]. Since then, SPTs have been conducted for a wide range of analytes in many different materials (Table 1). The targets sampled including soil, food (wheat, green coffee, lettuce, butter, apple juice), waste water, and air/atmospheres (in the workplace, stacks and landfill emission). The basic limitations of SPTs have recently been identified [4], but they can largely overcome by designing the SPT to meet a series of criteria [5]. The target can either be a batch of normal material, or it can be 'synthetic' with a known mass of the analyte added (Column 2, Table 1). In terms of who makes the chemical measurements, there are two options (Column 3 in Table 1). One option is for each participant to be responsible for the whole measurement process (i.e. sampling and their own analysis). The second option is that each participant is only responsible for their sampling, and the samples from all of the participants are collected by the organiser and submitted to one independent lab for analysis under repeatability conditions.

Newer *in situ* measurement techniques, such as portable-XRF for soil, pH sensors for water and IR spectrometry for gases, effectively combine the two traditionally separate processes of primary sampling and chemical analysis. SPTs using these *in situ* techniques are indicated in Table 1 (Column 3). Such PTs can potentially improve the quality of the whole measurement process, and might therefore be better described as Measurement Proficiency Tests (MPTs).

Table 1. Description of SPTs undertaken since first in 1995, showing range of sampling media and analytes (simplified from [4]). Synthetic sampling targets, and SPTs with centralized chemical analysis, are shown in bold. *In situ* measurements are shown in italic

Target Medium Synthetic target? (if in bold)		Analytes Central Lab? *In situ test?*	No. of Partici-pants	No. of rounds	Ref	Comment
Soil		Pb & Cu	9	1	[3]	First reported SPT realisation.
		Pb & Cu	9	2	[6]	Improved performance in second round.
	Soil	Ba	9	1	[7]	Spatial resolved SPT to locate 'hot spot'.
Air	Workplace	Hydrocarbons	38	3	[8]	Not 'SPT', no z-scores. Improved performance evident.
	Landfill-gas	*CH_4, CO_2, O_2*	9	1	[9]	Temporal variability corrected.
	Stack gas	*Gases* & particulates	4	?	[10]	Adapted homogeneity test for ISO 13528 compliance.
	Stack gas	*Gases*	15	16	[11]	Homogeneity to EN15259.
Food (bulk)	Wheat	N, Mo, Pb	5	1	[12]	All participants used same protocol.
	Coffee	H_2O	8	1	[12]	All participants used same protocol.
	Lettuce 'in field'	NO_3^-	16	1	[13]	First example of virtual SPT, with partici-pants from 16 different countries.
	Butter	H_2O	9	1	[5]	Used to estimate U, including between-sampler bias.
	Apple Juice	Patulin	9	1	[14]	Not all SPT design criteria were met.
Water	Water-waste	COD, TOC, *pH,Temp*	16-20	3	[15]	*In situ* measurement of pH &Temp.

The scoring of participants within an SPT, is analogous to that used in analytical PTs. A z-score is given to each participant, generally based upon $z = (x - x_{pt})/\sigma_{pt}$, for their measurement result x, an assigned value x_{pt}, and a fitness-for-purpose criterion σ_{pt}. In most SPTs, the assigned value is usually based upon a consensus value (e.g. the robust mean), but it can be based upon the known mass of analyte added to a synthetic sampling target.

The number of rounds in the SPT vary (Column 5, Table 1). In some sectors, such as food, only a single-round pilot SPT has demonstrated the feasibility of the approach. However, in other sectors, such as stack-gas and water sampling, regular ongoing

SPTs have been implemented and have proved clear improvements in the quality of the sampling [8], and hence also in the quality of the measurement values. The main reason for the difference in the extent of adoption of SPT between these various sectors, seems to be due to regulatory or accreditation requirements (e.g. ISO/IEC 17025 or 17020)

SPT results for uncertainty estimation

It has become increasing accepted that purely analytical PT results can been used to improve estimates of measurement uncertainty, by including the contribution from between-lab bias. Similarly, it was proposed in 1995 that SPT results could also be used to improve estimates of measurement uncertainty arising from all sources, by including the contribution from between-sampler bias [16]. This concept was demonstrated in practise in 2011 in an SPT on the determination of moisture (i.e. water) in butter [5]. The estimate of uncertainty, including the between-sampler bias, was shown to be nearly twice as large as the estimate made by applying the duplicate method to the sampling by a single sampler, even after excluding two non-proficient samplers.

2 FUTURE OF SAMPLING PROFICIENCY TESTING

Possibilities for improving the usefulness, and therefore uptake, of SPTs include :

a) Increase the acceptance of SPTs as an essential part of the accreditation of organisations and the certification of samplers.
b) Apply SPTs in new media/analyte combinations, including situations with *in situ* measurement devices to combine both sample and analysis.
c) Use SPT results to improve estimates of measurement uncertainty, by including both between-sampler and between-method bias, and compare against estimates made by other methods (e.g. duplicate method applied by single sampler)
d) More spatially-resolved SPTs (e.g. apply techniques in [7] to the micro-level)
e) Investigate temporally-resolved SPTs (e.g. to characterise an emission incident from an industrial release, into a river or the atmosphere)
f) Find ways of reducing the costs of implementing SPTs to increase uptake (e.g. sending out identical physical targets, or use a virtual target [13]),

3 CONCLUSIONS

Sampling proficiency test have proven applicable to a wide range of analytes in media in every different phase (gas, liquid and solid). The benefits of SPTs have been demonstrated by reducing the variability between sampler, and therefore reducing the measurement uncertainty arising from sampling. Further applications of SPTs are expected improve the reliability of measurements across an increased range of material, and to include newer techniques using *in situ* measurement devices.

Key words

Sampling proficiency testing, quality of sampling, measurement uncertainty

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